

DETERMINATION OF TECHNOLOGICAL PARAMETERS OF SELENIUM RECOVERY FROM METALLURGICAL PRODUCTION MIDDLEINGS IN A VACUUM-DISTILLATION UNIT

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ABSTRACT

The paper demonstrates the results of technological tests conducted with a representative rough selenium sample, obtained at Kazakhmys Smelting LLP to prepare refined selenium using vacuum-distillation technology, developed at the Institute of Metallurgy and Ore Benefication JSC, using the vapor phase filtration method on the existing process equipment. The technological scheme provides for preliminary melting of rough selenium in a receiving melting furnace and subsequent vacuum distillation of selenium. The vacuum-distillation recovery technological parameters are determined for selenium obtained from selenium-containing middleings produced by Kazakhmys Smelting LLP under conditions close to the production. We carried out the tests using the only industrial vacuum distillation unit prototype in the Republic of Kazakhstan. These tests enabled us to obtain refined selenium containing more than 99.5% of the main component with the throughout recovery 94.1%. The unit consists of the source material receiving smelting furnace and a vacuum distillation apparatus. The source material segregation process was implemented at atmospheric pressure and at 475 °C, and the resulting melt was filtered through a metal grid located on a false bottom in the receiving smelting furnace. Then, the ingots of selenium melted were sent to a vacuum distillation apparatus consisting of an evaporator and a condenser. We carried out the vacuum distillation of selenium remolded under optimal conditions: an evaporator temperature is 425 °C, a condenser temperature is 165 °C and residual pressure in the system is 0.4–1.1 kPa. Heating the condenser provided liquid-phase condensation of selenium vapor. The resulting refined selenium was cast into 5.0 kg bars. Besides, we obtained the free-flowing residuals enriched with precious metals during vacuum distillation with a silver content of 13 400 g/t. The free-flowing residue was 8.1%.

KEYWORDS: Selenium, Vacuum Distillation, Slurry, Industrial Products, Industrial Prototype, Processing, Extraction & Kaldo Furnace

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1. INTRODUCTION

The mankind's selenium use history dates back more than one hundred and thirty years [1,2]. Selenium is widely used in electronics, photographic equipment, metallurgy, rubber industry, organic synthesis and in the glass pro-

duction [3]. Selenium with at least 99.5% main component content corresponding to ST1 (selenium of technical) brand [4] and intended for export is in particular demand in the industry.

Table 1: The Chemical Composition of Selenium in Accordance with GOST 10298–79

Mark of Se	Chemical composition, %								
	Se, not less	Impurities, no more							
		Fe	Cu	Pb	Hg	Te	As	S	Al
ST0	99.8	0.005	0.002	0.002	0.001	0.05	0.003	0.005	0.005
ST1	99.0	0.01	0.005	0.005	0.005	0.1	0.005	0.02	0.005

Table 1 shows the chemical composition of selenium according to the main regulated additions per GOST 10298-79 [4].

In the earth's crust, the content of selenium is $6 \cdot 10^{-5}$ wt. %, it refers to rare scattered elements. World reserves of selenium are estimated by the American Geological Survey (USGS) at 80–90 thousand tons [5]. Large reserves of selenium include hydrothermal sulfide deposits, such as polymetallic, copper-zinc, pyrite, and copper-molybdenum. In 2015, selenium reserves in the fields amounted to, thousand tons: China - 26.0; Chile - 25.0; Russia - 20.0; Peru - 13.0; USA - 10.0; Canada - 6.0; Poland - 3.0; other countries - 21.0; total reserves - 120.0.

Under USGS estimates [5], the world selenium consumption is 40% in metallurgy (including manganese production), 25% in glass production, 10% in agriculture, 10% in chemicals and pigments production, 10% in electronic industry and 5% in other industries. The main selenium production source is sulfuric acid, pulp, and paper production wastes burnt, and anode sludge from copper anode plants processed [1,6]. Selenium dioxide (SeO_2) generated is reduced with sulfur dioxide gas (SO_2) to elemental selenium brought to a graded condition with the help of recrystallization, vacuum distillation, hydride and other methods [7].

The total production of selenium is estimated at approximately 3,000 tons/year; only about 20 of the approximately 80 copper enterprises in the world, report that they receive selenium or collect sludge to extract selenium. Sludge from the electrolytic cleaning of copper anodes contains 5-25% selenium in the form of compounds with noble metals; therefore, the main task of technologists is to extract gold and silver, and only then selenium (according to the technology, factories extract Se first, and then the Dore alloy: Au-Ag).

Selenium is mainly used in semiconductor technology to manufacture rectifiers and photocells, in the glass industry to bleach green glass and to produce ruby glasses, in the vulcanization of rubber, in the photographic industry and in the manufacture of some optical and signal devices, in the steel industry - as a modifier for casting steel fine-grained structure, improving the mechanical properties of stainless steels, in the chemical industry - as a catalyst, in the pharmaceutical industry, and other industries [5].

In metallurgy, selenium is added (up to 1%) to alloys based on iron or copper to increase their strength and plastic properties. Selenium-doped lead is used to make battery gratings. In magnesium-manganese alloys, the addition of 0.3–0.5% selenium improves non-corrosion property. In China, the production of electrolytic manganese has become a noticeable area of selenium application: Se_2O_3 is added to the bath during manganese electrolysis.

The main world consumers of technical selenium are enterprises in Japan, China, and India.

The selenium high activity results in the difficulty of its purification against most impurities [8]. Different flow diagrams and industrial equipment enabling to increase the quality and quantity of the commercial selenium produced [9] are being developed to solve this problem.

Arsenic, mercury, bismuth, copper, nickel, tellurium, and sulfur are especially undesirable impurities in selenium. It was found that the impurities of many metals introduced in the form of selenides, even in small concentrations (0.1-0.01 wt.%), Cause a weakening of the rectifying action of rectifiers [10]. So, for example, copper and nickel sharply lower the coefficient of straightening.

The main source of selenium is sludge from copper processing plants [11].

The Republic of Kazakhstan is one of the largest regions in the world that possess large reserves of rare and rare-earth metals [12]. Due to solar cells, lasers, LEDs and photodetectors production growth, selenium has become a strategically important raw material. The main commercial selenium producers in Kazakhstan are Corporation Kazakhmys LLP and Kazzinc LLP. However, these metallurgical giants of the Republic obtain off-grade selenium as a by-product of the main production that is substantially cheaper than the branded ones playing a major role in the semiconductor and high-tech industry development [13]. Almost the entire volume of technical selenium produced in the Republic of Kazakhstan is exported to China at low prices.

When obtaining selenium at Kazakhmys melting LLP, a subsidiary of Kazakhmys Corporation LLP, precious metals are extracted from the anode sludge formed in blister copper electrolysis shops [14,15]. The process is as follows: sludges are decoppered and smelted in a Kaldo furnace that combines several operations (roasting, melting, recovery and conversion) and enables to produce Dore metal containing up to 97% silver and more than 2% gold [16]. Selenium is recovered from the exhaust gases from the Kaldo furnace. Gold is separated from silver by electrolysis [17]. Kazakhmys melting LLP has gas and water treatment departments. The final products are gold in bullions with a purity of 99.99% and pelleted silver with a purity of 99.96 to 99.99%, rough selenium and cuprous telluride.

The Kaldo furnace is a compact and energy-efficient high-performance reactor. Heating is provided by a refining oxyfuel lance. At the conversion and recovery stages, a special lance is used to supply air at supersonic speed, thereby ensuring high oxidation efficiency.

When the Kaldo furnace runs, all exhaust process gases pass through a gas recovery and purification system. Selenium from the sludge passes into the gas phase by almost 98%.

Leaving the Kaldo furnace process gases enter the Venturi system consisting of a cooling tower, a Venturi scrubber and a cyclone separator. In the Venturi system, gases are cooled due to the water evaporation from 600 to 60–70°C. Then, the gases enter the second stage - the Venturi scrubber consisting of a confuser (tapering cone), a neck (narrowed cylindrical chamber) and a diffuser (expanding cone). After the venturi scrubber, the gas enters the cyclone separator. Through a smoke exhauster, gas from the gas treatment unit is sent to a wet electrostatic precipitator. To remove droplets after a wet electrostatic precipitator, gas is directed to a spray trap, bag filter and then thrown through a smoke exhauster into a chimney [16].

During gas capture in the circulating solution, not only dust is participated, but some gases (selenium dioxide and arsenic trioxide) are dissolved, also some metal chlorides are absorbed.

After all process gases trapping and purifying stages, pulp is formed in the circulation tanks containing: 40–50 g/L of solid; the solution contains 20–50 g/L of selenium, 2–5 g/L of chlorine (pH = 0-1). Volume: 10–15 m³.

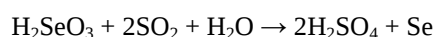
At the first stage of the selenium production technology, the task is to leach residues of water-soluble selenium from the sludge. To do this, the pulp in the tank is stirred for 30 minutes. Then, the solution is checked for the presence of

silver; if silver is detected, copper powder is added to the solution until silver is completely cemented. Then sodium hydroxide is added to the pulp to increase the pH of the suspension up to 8–9. At this pH, all impurities precipitate in the form of hydroxides.

After the deposition of hydroxides, the content of copper and lead in the solution must be determined. The process is considered complete if the residual content of these components does not exceed 0.01 g/L. Then, the precipitate must be separated on the filter press; it should not be washed to avoid redissolution of impurities that have precipitated. The deposit must be dried only with compressed air. This deposit is called Venturi sludge, it is a repetition material and is processed in the Kaldo furnace.

The filtrate enters the tank of the first stage of selenium deposition, where it is heated to a temperature of 70°C at which the supply of gaseous sulfur dioxide begins. The solution continues to be heated, since the optimum deposition temperature of selenium is 78 to 82°C [1] and should be maintained precisely in this range during deposition, which is ensured automatically.

At this stage, sulfur dioxide is supplied for 6 to 10 hours. Selenium precipitates as a result of the following reaction [2]:



Utilization coefficient for sulfur dioxide is approximately 100% if a selenium content in solution is up to 1 g/L; the coefficient decreases to 10% if a selenium content is 0.1 g/L.

The precipitation of selenium must be carried out until a deposit with a selenium content of at least 85% is obtained. Upon receipt of such a deposit, the process is stopped and the pulp is sent for filtration to a filter press. Selenium on the filter is washed to a residual sulfuric acid content of not more than 0.2% in the deposit. The deposit is dried on a filter press with compressed air. This selenium is considered commercial, however, on the basis of the interstate standard GOST 10298–79 in force in the Republic of Kazakhstan [4], it is not branded and is not quoted on international metal exchanges, i.e. selenium of such purity is non-standard.

The filtrate, combined with the wash water enters the tank of the second stage of precipitation of selenium. At this stage, the goal is to deeply extract the residual selenium and obtain its required content in the solution, which is sent to water treatment.

In the process gases of the Kaldo furnace, almost all selenium is present in the form of SeO_2 , but its small amount is also contained in the form of SeO_3 . Selenium in this form does not deposit as sulfur dioxide (SO_2). Therefore, at low concentrations of selenium (IV) and for the precipitation of selenium (VI), thiourea is used, which is given in dry form until a solution with selenium content of less than 0.02 g/L is obtained [18,19].

Then, the pulp is filtered on a filter press, the deposit is washed with a small amount of water and dried with compressed air. This deposit is considered rough selenium, it is a repetition material and is processed in the Kaldo furnace.

Rough selenium obtained in the precious metal shop of the Balkhash smelter is a finely divided, wet, pelletized black (dark gray) material containing residues of selenic and sulfuric acids.

The economic situation in the world requires to obtain quality products with high added value. The world copper prices collapse [20] helped to the management of Kazakhmys Corporation LLP to decide to obtain refined selenium instead of rough one at Kazakhmys Smelting LLP.

The authors' efforts are aimed to implement the environmentally friendly technology, developed to obtain the branded selenium at the Balkhash Copper Smelter production facilities of Kazakhmys Smelting LLP.

2. RESULTS OBTAINED

The vacuum-distillation technology for rough selenium refinement using a vapor filtration method [21] was developed, and an industrial prototype of the unit [22] was created for its practical implementation in the vacuum processes laboratory at Institute of Metallurgy and Ore Beneficiation JSC. Implementation of the process in a sealed apparatus makes the ingress of toxic elements in the environment impossible. The environmental effect was provided with the use of vacuum equipment that has no emissions into the environment and complying with international environmental standards.

The paper demonstrates the results of technological tests conducted with a representative rough selenium sample obtained at Kazakhmys Smelting LLP to prepare refined selenium using vacuum-distillation technology developed on the existing process equipment.

We carried out the technological tests with a representative rough selenium sample obtained at Kazakhmys Smelting LLP. There is the following element content in the source material, under the quality certificate for rough selenium of refining production issued by the precious metal workshop in Balkhash copper-smelting plant of Kazakhmys Smelting LLP, wt. %: 93.33 - Se; 0.0002 - Au; 0.04 - Ag.

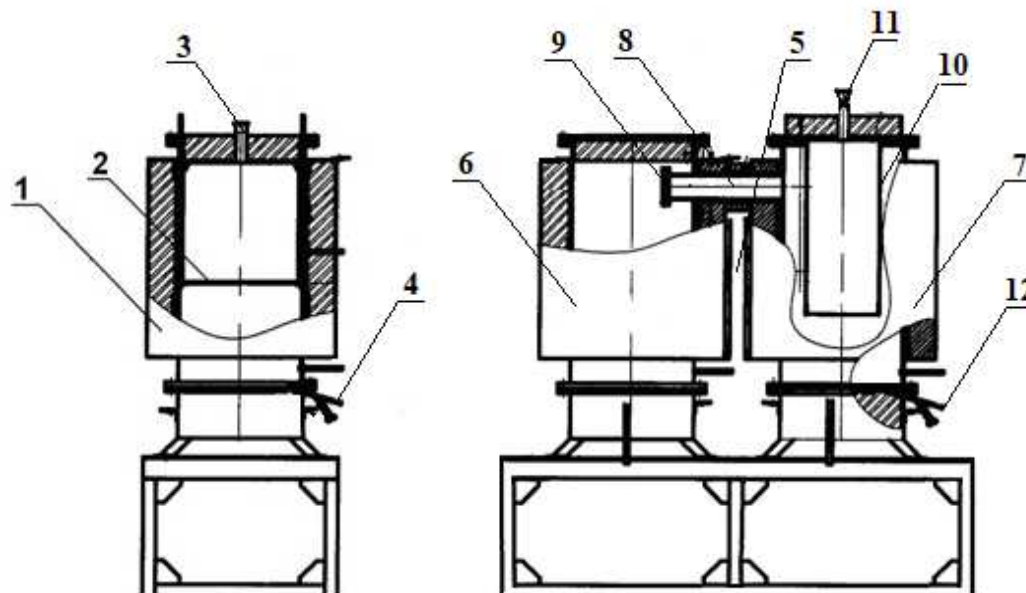
The moisture content of the starting material is determined by the gravimetric method according to the standard method. The moisture content of the source material was 18.78%; the pH of the condensate collected during source material drying was 1.63. The bulk density of the dried rough selenium was 1.7 kg/cm³ without a shakedown run, it is 2.12 kg/cm³ with a shakedown run, the repose angle is 47°. The following elemental content was determined using the Axios "PANalytical" X-ray fluorescent wavelength-dispersive combined spectrometer, wt. %: 89.511 - Se; 2.032 - O; 1.594 - S; 0.766 - Mg; 0.759 - Na; 1.684 - Pb; 0.311 - Al; 1.011 - Te; 1.595 - Cl; 0.101 - Ag; 0.109 - Si; 0.199 - Sb; 0.131 - Cu; 0.112 - Fe; 0.003 - P; 0.082 - As.

X-ray phase analysis carried out using the D8 Advance (BRUKER) apparatus in cobalt radiation identified the following main phases in the source rough selenium: Se (Selenium); AsSe₉Cu_{0.05} (Copper Arsenic Selenide); CSe₂ (Carbon Selenide).

The figure shows the apparatus diagram of an industrial vacuum distillation unit prototype. The unit consists of the source material receiving smelting furnace and a vacuum distillation apparatus. The source material segregation process was implemented at atmospheric pressure and at 475 °C, and the resulting melt was filtered through a metal grid located on a false bottom in the receiving smelting furnace.

This operation allows you to remove moisture from the material and separate selenium from possible intermetallic impurities. For an approximate gas phase composition determination during drying and melting of rough selenium, the outlet pipe of the in-take melting furnace was connected to a water-cooled cooler-type heat exchanger equipped with a condensate-holding tank in the lower part serving as a water seal. The condensate collected in the heat exchanger contained an insignificant amount of solid suspension, so it was filtered; the filtrate was sent for X-ray analysis, and the dried solid suspension was sent for X-ray fluorescence analysis. The acidity of the filtrate was measured on a pH-150 M instrument. During technological tests, pH of the collected condensate moisture was 2.22. X-ray analysis showed that, along with water, the condensate contains sulfur and sulfuric acids. An X-ray fluorescence analysis of a solid suspension of steam condensate formed at the

outlet of the in-take melting furnace showed that it contains the same elements as the feedstock. This indicates the mechanical removal of particles from the furnace by an intense vapor stream. The melt of remelted selenium was released through a needle valve into the molds located at the bottom of the furnace.



1 - Receiving Smelting Furnace; 2 - "False Bottom"; 3 - Gas Flue; 4 - Needle Valve; 5 - Vacuum Distillation Apparatus; 6 - Evaporator; 7 - Condenser; 8 - Steam Line; 9 - Filter; 10 - Steam Trap; 11 - Connection of the Vacuum Pump; 12 - Needle Valve to Drain Refined Selenium.

Figure 1: Diagram of the Vacuum-Distillation Unit for Se Refining.

Then, the ingots of selenium melted were sent to a vacuum distillation apparatus consisting of an evaporator and a condenser. We carried out the vacuum distillation of selenium preliminary remelted under optimal conditions previously defined [21], i.e. an evaporator temperature is 425 °C, a condenser temperature is 165 °C and residual pressure in the system is 0.4–1.1 kPa.

After loading the source material into the vacuum distillation apparatus, the heating of the evaporator started. After reaching a temperature of 300°C in the evaporator, the vacuum pump is turned on and the condenser heaters are turned on. The vacuum pump is included in the system through a bag filter which is installed directly in front of the vacuum pump. The bag filter is designed to capture finely dispersed selenium which can possibly blow on through in small quantities in conditions of volumetric condensation. Due to the directed removal of the gas phase from the system (operation of the vacuum pump), selenium vapor passes through the steam line into the condenser. A cartridge with a special design filter is installed in the steam line connecting the evaporator and the condenser, which ensures the purification of gaseous selenium from impurities of refractory impurity elements mechanically carried out by the steam stream into the condenser.

Due to the temperature difference in the evaporator and the condenser, volumetric condensation of selenium occurs in a lower-temperature zone in the condenser. The operating temperature of the condenser provides liquid-phase condensation of selenium which flows into the bottom base of the condenser and is in a liquid state. The distillation process lasts approximately 6 to 8 hours.

The vacuum distillation apparatus is designed so that the ratio of evaporation area to condensation area is 1:8, and the ratio of evaporation area to the cross section of the steam line connecting the evaporator and condenser is 3:1.

Table 2: Material Balance of the Selenium Distribution by Products in the Receiving Smelting Furnace Segregation Process

Products name	Weight, kg	Dry weight, kg	Output, %	Se Content		Distribution, %
				%	kg	
Loaded:						
Rough Se	18.2	14.78	100.00	89,51	13.23	100.00
Obtained:						
SegregatedSe	10.94	10.94	74.02	95.61	10.57	79.90
Slag	3.49	3.49	23.61	62.21	2.17	16.40
Total obtained	14.43	14.43	96.28	—	12.74	96.30
Discrepancy:	—	-0.35	-2.37	—	-0.49	-3.70

At the time of the onset of intense evaporation of selenium, a slight increase in pressure in the system occurred (by 1.33–2.66 kPa, 10–20 mm Hg). The completion of the process was determined by a decrease in pressure in the system - less than 0.13 kPa (less than 1 mmHg).

The resulting refined selenium was cast into 5.0 kg bars and was tested for the content of impurity elements by X-ray fluorescence analysis.

18.2 kg wet source selenium was dried and segregated in a receiving smelting furnace resulting in the removal of moisture from the material, then the melted selenium was filtered through a metal 0.45x0.45 mm grid installed on a false bottom.

We obtained 10.94 kg selenium ingots containing 95.61 wt. % of the main component later subjected to distillation in an industrial vacuum distillation unit prototype. The 3.49 kg grid residue, the so called “slag”, contained 62.21 wt. % of selenium.

X-ray fluorescence analysis method for remelted selenium in ingots determined the following element content, wt. %: 95.611 - Se; 1.639 - O; 0.371 - S; 0.238 - Mg; 0.296 - Na; 0.465 - Pb; 0.077 - Al; 0.621 - Te; 0.516 - Cl; 0.011 - Ag; 0.071 - Si; 0.032 - Sb; 0.021 - Cu; 0.031 - Fe, i.e. When the melt is filtered through a metal mesh with a mesh size of 0.5 x 0.5 mm, a significant purification of selenium from impurity elements occurs. Table 2 shows the material balance of the selenium distribution by products in the receiving smelting furnace segregation process.

The remelted, filtered selenium output was 74.02%, slag output was 23.61%, while the balance discrepancy under solid products was -0.35 kg (-0.37%), and it was associated with the conventionally constant selenium amount located in the form of the skull at the bottom of the receiving smelting furnace. The selenium distribution by processing products was 79.9% of selenium passed into the melt (ingots obtained) and 16.4% of selenium remained in the slag.

The slag obtained as a result of in-take melting was a agglomerated, sintered material, which was relatively easily separated from the inner walls and the false bottom of the furnace.

In individual samples of slag, the content of the prevailing impurity elements, determined by X-ray fluorescence analysis, varied within the following limits, mass. %: 2.279-6.236 Na; 1.479-10.625 S; 1.099-1.864 Te; 0.628-1.026 Pb; 65.88-98.86 Se.

During the tests performed, it was found that when combining the drying of material with high humidity and melting of the material, the process is characterized by a significant duration and high specific energy consumption. The specific energy consumption in melts ranged from 2.56 to 4.77 kWh/kg of remelted selenium, and its maximum values were obtained at lower temperatures (395-415°C).

Table 3: The Material Balance of the Selenium Distribution by Vacuum Distillation Products

Products Name	Dry weight, kg	Output, %	Se content		Distribution, %
			%	kg	
Loaded:					
Melted Se	10.94	100.00	95.61	10.57	100.00
Obtained					
RefinedSe	10.51	96.07	99.54	10.46	98.96
Dry residue	0.08	0.73	—	—	—
Total obtained	10.59	96.80	—	10.46	98.96
Discrepancy:	-0.35	-3.20	—	-0.11	-1.04

We determined the silver content in the products obtained after the segregation process in the receiving smelting furnace using the X-ray fluorescence analysis method and amounted to wt. %: 0.393 - in the slag; 0.011 - in melted selenium. Thus, 91.76% of silver contained in the source rough selenium passed into the slag.

10.57 kg of refined selenium was obtained with 99.54% content of the main component corresponding to the ST1 brand under GOST 10298-79 [4] intended for export, as a result of vacuum distillation of the remelted rough selenium obtained (10.94 kg).

Table 3 shows the material balance of the selenium distribution by the products of vacuum distillation of ingots, obtained from the liquation of the source rough selenium in the receiving smelting furnace.

X-ray fluorescence analysis method for refined selenium in ingots determined the following element content, wt. %: 99.543 - Se; 0.217 - O; 0.003 - S; 0.003 - Pb; 0.021 -Mg; 0.007 - Ni; 0.005 - Al; 0.122 - Te; 0.005 - Cl; 0.003 -Si; 0.031 - Sb; 0.033 - Cr; 0.002 -Cu; 0.005 - Fe. The refined selenium output was 96.07%. 98.96% selenium was transferred to raffinate. Selenium is not detected in the bulk residue from the distillation, while the silver content was 2.05 wt. %

Thus, the tests of the technology developed without the preliminary material washing stage and its subsequent drying showed the applicability of the process equipment to obtain refined selenium with a weight fraction of the main component of more than 99.5% within one stage.

Vacuum distillation tests for slags obtained in the rough selenium segregation process in a receiving smelting furnace were carried out to determine the possibility to recover more selenium from the source raw material. The x-ray fluorescence analysis method used in the slag study determined the following content of elements, wt. %: 62.212 - Se; 3.639 - O; 5.616 - S; 5.251 - Mg; 2.321 - Na; 5.731 - Pb; 1.089 - Al; 2.378 - Te; 5.185 - Cl; 0.394 - Ag; 0.258 - Si; 0.733 - Sb; 0.481 - Cu; 1.864 - Fe; 0.029 - P; 1.011 - As.

The 3.49 kg source slag containing 2.17 kg of metallic selenium was loaded into a vacuum distillation apparatus.

The slag was distilled in an evaporator at 535–550 °C and 0.4–0.9 kPa. The condenser heaters were disconnected during the distillation period, while the condenser walls temperature was 180–195 °C. 2.01 kg selenium with the main component content of 99.01% and 1.39 kg of a bulk residue with a selenium content of 2.88% were obtained after the distillation. Table 4 shows the material balance of the selenium distribution by products after slag vacuum-distillation processing.

The selenium output after slags vacuum distillation was 57.59%, while 91.71% selenium was transferred to condensate. Selenium obtained from slag vacuum distillation was identified by the X-ray fluorescence analysis method for compliance with the ST1 brand according to GOST 10298-79 [4]. The main impurities content does not exceed the values for ST0 grade selenium except for the Te impurity that is difficult to be removed by vacuum distillation with the content 0.089% in the condensate while the Te content in the source material (slag) was more than 2%.

Table 4: Material Balance of the Selenium Distribution by Products after Vacuum-Distillation Processing of Slags Obtained from Material Segregation in a Receiving Smelting Furnace

Products Name	Dry weight, kg	Output, %	Se content		Distribution, %
			%	kg	
Loaded:					
Liquation slag	3.49	100.00	62.21	2.17	100.00
Obtained					
RefinedSe	2.01	57.59	99.01	1.99	91.71
Dry residue	1.39	39.83	2.88	0.04	1.84
Total obtained	3.40	97.42	—	2.03	93.55
Discrepancy:	-0.09	-2.58	—	-0.14	-6.45

The dry free-flowing residue output was 39.83% with 1.84% selenium transferred. The vacuum distillation product discrepancy was minus 0.09 kg or minus 2.58%. X-ray phase analysis revealed AgSe presence that does not decompose or sublimate at distillation temperatures [1], in the bulk residue.

The following elements were determined by X-ray fluorescence analysis in the dry residues, wt. %: 5.83 - Na; 5.33 - Mg; 14.11 - S; 2.91 - Fe; 1.84 - Sb; 3.97 - Te; 14.39 - Pb; 1.21 - Cu; 0.981 - Ag; 2.086 - As; 2.88 - Se. Dry residues are quite easily removed from the evaporator using an industrial vacuum cleaner.

To define the silver amount in the bulk residue, we subjected the latter to nitrate leaching (liquid to solid = 1:1) to convert silver into the solution. The solution obtained was filtered, the residues were washed with distilled water. Dissolved silver in AgCl form was precipitated from the resulted solution by hydrochloric acid addition. The silver chloride was filtered off, washed, and dried to a constant weight. The silver content in the amount of 1.34% (13.400 g/t) was determined by recalculating the weight of AgCl obtained [23]. The yield of solids was 8.1%.

It should be noted that frequent oil replacement in a vacuum pump was required for slag distillation due to selenium dioxide coagulation in it, that was determined in vacuum oil using an IR spectrophotometry analysis (selenous acid ions $[\text{SeO}_3]^{2-}$ presence was determined).

Selenium recovery from the receiving melting slags by vacuum distillation enables to increase its throughput recovery up to 94.1%, however, it significantly increases energy consumption and, accordingly, the redistribution cost. In this regard, it is most expedient to send receiving smelting slags containing precious metals with the output of ~ 20% in a significant amount to the process started, to the Kaldo furnace, to reextract selenium from them. This technological approach will provide more stable operation of vacuum equipment and reduce the selenium and precious metals loss with a number of resulting processing middlings of standard grade selenium (secondary sublimates and residues).

3. CONCLUSIONS

Technological tests of the technology developed were carried out without a preliminary stage of source material washing against water-soluble impurities and residual acid content and its subsequent drying. The presence of residual acid content in the starting material causes corrosion of the furnace elements. And, the high humidity of the source material dramatically increases the energy costs of processing. The vacuum distillation apparatus is designed to transfer selenium into the vapor phase, followed by its filtration and condensation of selenium in a lower-temperature zone. The principle is based on the difference in vapor pressure of selenium and other elements. In this case, “non-volatile” impurities remain in the evaporator, and selenium condensed in the condenser is poured into the molds after the end of the process.

The process equipment applicability was confirmed to obtain refined selenium during one stage with a weight fraction of the main component of more than 99.5%. The selenium recovery from rough selenium preliminary melted in the receiving melting furnace with vacuum distillation was 98.96%. During technological tests, all technological vacuum equipment worked stably and reliably.

Tests have shown that in this raw material, tellurium is the most difficult impurity separated by physical methods. Therefore, to obtain refined selenium of higher grades, selenium-containing solutions must be purified from tellurium by hydrometallurgical methods before selenium recovery. During the refining of remelted selenium, a dry residue remains in the evaporator, in which noble metals are concentrated.

The silver main amount (more than 95%) is concentrated in the slags formed during the source material segregation process in the receiving melting furnace.

Technological tests were carried out to obtain branded selenium from non-conforming selenium, i.e. selenium-containing slags obtained during source rough selenium segregation in the receiving melting furnace. Although selenium recovery from the received melting slags with vacuum distillation enables to increase its throughput recovery up to 94.1%, it results in noticeable corrosion of the structural material in the equipment and the need for frequent oil changes in the vacuum pump disrupting the stability and reliability of the entire equipment. In this connection, it is advisable to send slags from the receiving smelting into the Kaldor furnace to re-extract selenium and precious metals from them.

It should be noted that dispersed dry residues easily removed from the evaporator were obtained during the vacuum distillation refining of dry non-standard selenium. When combining the process of in-take melting and drying of rough selenium, energy consumption increases significantly. If during direct distillation of dried rough selenium and distillation of re-melted rough selenium, the specific energy consumption has comparable values, then when in-take melting of the same material at high humidity, it increases by 3 to 4 times. In this regard, in each particular case, it is necessary to calculate the economic feasibility of the process either with the combination of drying and in-take melting, or with preliminary drying of selenium-containing feedstock in thin layers in dryers.

In this work, refined selenium was obtained in the form of ingots.

Selenium can be obtained, at the request of the consumer, both in the form of granules and in the form of a powder. To obtain granules, selenium ingots are loaded into a granulator, where it is brought to its melting point at atmospheric pressure. Then, the selenium melt is released through a heated needle valve into container with distilled water. To obtain a given granule size, nozzles with the corresponding diameter are worn on the outlet of the needle valve. To obtain powdered selenium, the granules are crushed in a ball mill. To prevent selenium contamination with impurity elements, ceramic balls are used as abrasive elements in the mill.

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